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Dynamics of Reactions Involving Hydrogen Atom or Proton Transfer. Symmetric Case

by

V. K. Babamov

and

R. A. Marcus

R. A. Marcus
Principal Investigator

Dynamics of Reactions Involving Hydrogen Atom or

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V. K. Babamov and R. A. Marcus[a]

Arthur Amos Noyes Laboratory of Chemical Physics,

California Institute of Technology, Pasadena, California 91125

(Received

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FOREWORD

The reactive transfer of a light particle such as a proton or hydrogen atom is of interest in the electrochemical hydrogen evolution reaction and in other systems. In the present report an approximate method is formulated for treating the reaction dynamics of transfer of a light particle. A particular intermolecular potential is considered to permit comparison with exact numerical quantum mechanical results for the transfer probability. The results are in good agreement and the method thereby provides a new tunneling description for the light particle. The present report is restricted to the case of a symmetric reaction, $AH + A \rightarrow A + HA$. The work is being extended to asymmetric reactions $AH + B \rightarrow A + HB$.

I. INTRODUCTION

In low energy thermoneutral or nearly thermoneutral reactive collisions, only one vibrational state is often possible in both reactants and products and the vibrational quantum number appears conserved. For these (and other) collisions quasi-constants of the motion may exist which remain approximately conserved throughout the collision. If such a quasi-constant of the motion can be found for a particular reaction, usually in the form of a suitably defined generalized vibrational quantum number, it can improve the understanding of the dynamics of the reaction and facilitate its computational treatment.

If a quasi-constant of the motion does exist for a particular reaction one of the ways of finding it is to find a set of coordinates in which the Hamiltonian is nearly locally separable and one of the coordinates represents a generalized vibration which remains to a large extent in the same quantum state throughout the collision.

One approach of this kind is based on the near-separability of the potential energy surfaces for some reactions in the vicinity of the minimum energy path from reactants to products. In terms of "natural collision coordinates",[1] designed to take advantage of such near separability of the potential energy surface, the vibration of the reactants gradually changes its character during the collision to become a vibration of the products, passing through a symmetric stretch vibration or the collision complex. Such a near-separation is expected to be most suited, other things being equal, to collisions in which the minimum potential energy path has a low curvature in the usual mass-weighted Cartesian coordinate space.[2] It has been useful for treating a variety of other reactive collisions.[3]

One class of reactions, the exchange of a light particle between two heavy ones, has radically different dynamical features and should be given a different treatment. The "reaction path curvature" is typically large in some regions because of the acuteness of the skewed angle in the usual mass-weighted coordinate plot for this reaction class. The large difference in masses in this case points to an effective Born-Oppenheimer[4] type adiabatic separation between the motion of the light atom relative to any of the heavy particles and the relative motion of the heavy particles.

The adiabatic separation of the motion of heavy and light atoms has been successfully utilized in finding eigenvalues of hydrogen bonded systems.[5] In collision problems a closely related approximation of treating the heavy particles' motion classically and the light particle motion quantum mechanically has also been used.[6] A semiclassical treatment which utilizes essentially the same dynamical features to simplify the expressions for the classical S-matrix has also recently been developed.[7]

In the present paper the adiabatic separability of the light atom motion from the heavy atom motion is used to simplify the quantum mechanical treatment of reactive collisions which involve exchange of a light particle, usually a hydrogen atom or a proton, between two heavy ones. Only the symmetric exchange of hydrogen atom between two heavier atoms is treated in detail in the present paper. Simple approximate expressions for the reactive transition probability in the ground vibrational state are derived. The non-symmetric case will be discussed in a later paper.

The Schrödinger equation for the system and the coordinate system in which the adiabatic separation can be utilized are presented in Sec. II. The transformation of the Schrödinger equations into a set of coupled ordinary differential equations in the adiabatic representation is given in Sec. III. The symmetric exchange case and the adiabatic approximation which leads to a simple expression for the reactive transition probabilities are given

in Sec. IV. A semiclassical limit expression, valid under certain conditions,
is derived from the quantum mechanical result in Sec. V. Calculations of the
transition probabilities for two model potential energy surfaces are given in
Sec. VI. A discussion of the treatment, its possible extensions, and a classical
path approximation are given in Sec. VII. The principal equations in
the paper are Eqs. (4.10), (5.7), (5.11), and (7.5).

II. SCHRÖDINGER EQUATION AND THE COORDINATE SYSTEM

Ths Schrödinger equation for a collinear reactive atom-diatom collision
$AB + C \rightarrow A + BC$ can be written, after separating the center of mass motion,
in atomic units as:

$$\left[-\frac{1}{2M_\alpha} \frac{\partial^2}{\partial R_\alpha^2} - \frac{1}{2m_\alpha} \frac{\partial^2}{\partial r_\alpha^2} + V(r_\alpha, R_\alpha) \right] \psi = E\psi, \quad \alpha = 1, 2 \qquad (2.1)$$

where r_1 is $Z_B - Z_A$, (Z denotes position along line), R_1 is $Z_C - Z_{AB}$, where
Z_{AB} is the position of the center of mass of the AB molecule, and m_1 and M_1
are the corresponding reduced masses. The subscript 2 refers to the same
quantities for the reverse reaction. So r_2 is $Z_C - Z_B$ and R_2 is $Z_{BC} - Z_A$,
Z_{BC} being the position of the center of mass of the BC molecule.

For systems with $M_\alpha \gg m_\alpha$ ($\alpha = 1, 2$) at low energy a Born-Oppenheimer[4]
type adiabatic separation of the hydrogen atom motion (along r_α) and the heavy
particle motion (along R_α) may exist and can be utilized to develop an approxi-
mate solution.

In order to simplify the derivation it is convenient to mass-weight[8]
the coordinates in (2.1) as

$$x_\alpha = M_\alpha^{\frac{1}{2}} R_\alpha; \quad y_\alpha = m_\alpha^{\frac{1}{2}} r_\alpha \quad (\alpha = 1, 2) \qquad (2.2)$$

The resulting typical shape of a potential energy function for a collinear arrangement of two heavy atoms with a light one between them plotted in mass-weighted coordinates is shown on Fig. 1 as a contour plot. The sharp angle γ between the axes on the plot is due to the large ratio of the scaling factors in (2.2), i.e., to a large mass ratio M_α/m_α and is given by

$$\gamma = \tan^{-1} m_B / (M_\alpha m_\alpha)^{\frac{1}{2}} \quad , \tag{2.3}$$

where m_B is the mass of the middle atom B. When $M_\alpha/m_\alpha \gg 1$ the angle γ for a symmetric reaction is approximately $(2m_B/m_A)^{\frac{1}{2}}$.

The Schrödinger equation in coordinates (2.2) becomes

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + V(x, y) \right] \psi = E\psi \quad , \tag{2.4}$$

It is the same as the Schrödinger equation with mass 1 moving in a two-dimensional potential field $V(x, y)$. The characteristic feature of the shape of the potential energy function in mass-weighted coordinates is the existence of two long narrow almost parallel channels (Fig. 1). The motion of the particle along the channel length corresponds largely to the relative motion of the two heavy particles, while across each channel it corresponds to the motion of the light particle relative to one of the heavy atoms.

The relevant features of the potential energy surface in coordinates (2.2) which lead to vibrational adiabaticity can be illuminated by plotting an example of a low energy reactive classical trajectory for a symmetric hydrogen atom exchange reaction shown in Fig. 1. The vibrational state of the system, i.e., the classical action variable for the motion parallel to the channel width, remains largely unchanged during the slow approach of

the reactants, due to the very moderate change of the profile of the bottom of the well over a vibrational period of the trajectory. Subsequently, the AB vibration can be viewed as being transformed briefly (for a half a vibrational period) into an asymmetric stretching vibration of the ABC complex, when the trajectory passes from the reactants' channel into the products' one. Once in the product valley the trajectory remains in the same vibrational state during the separation of the heavy atoms. This state is also the same as the initial one due to the exact matching of the reactant and product vibrational potential wells.

At large distances between the colliding partners the reactant and the product vibrational states are uncoupled from each other and the eigenfunctions χ of the vibrational part of the Hamiltonian can be used to construct the asymptotic solution to the Schrödinger equation.

$$\left[- \frac{1}{2} \frac{d^2}{dy_\alpha^2} + V(x_\alpha, y_\alpha) \right] \chi_i^\alpha (y_\alpha) = \epsilon_i^\alpha \chi_i^\alpha (y_\alpha) \quad (\alpha = 1, 2) \ . \quad (2.5)$$

The value of $\alpha = 1$ refers to the reactants' channel and $\alpha = 2$ to the products'. At sufficiently large R_1 and R_2, one has

$$\psi = \sum_{\alpha=1}^{2} \sum_{i} \phi_i^\alpha (x_\alpha) \chi_i^\alpha (y_\alpha) \ . \quad (2.6)$$

where $\phi_i^\alpha (x_\alpha)$ is the wavefunction for the x_α motion. The sum over i is over all asymptotic states in channel α.

In order to transform the Schrödinger equation into a set of ordinary differential equations which can be used to generate solutions of type (2.6) for large x_α one needs a pair of curvilinear coordinates which can be made arbitrarily close to x_α, y_α near the bottom of each valley of the potential energy surface, for sufficiently large x_α.

Several sets of coordinates with those properties have been proposed in the literature.[9-13] In this paper the polar coordinates[12, 13]

$$\rho = (x_\alpha^2 + y_\alpha^2)^{\frac{1}{2}}: \qquad \theta = \tan^{-1}(y_\alpha / x_\alpha) \tag{2.7}$$

which provide a combination of nearly optimal separability and extremely simple form of the Hamiltonian will be used.

For large ρ and moderate y_α one has

$$\rho \cong x_\alpha \tag{2.8}$$

and the vibrational coordinate y_α is most conveniently expressed in terms of the arc length along a circular arc with origin at $x_\alpha = X_\alpha = 0$.

$$s = \rho\theta , \qquad (\rho \rightarrow \infty) , \tag{2.9}$$

namely at large values of ρ one has

$$y_1 \cong s; \qquad y_2 \cong \rho\gamma - s . \tag{2.10}$$

(This $\underline{s}$ is not the $\underline{s}$ in Ref. 1.)

III. COUPLED CHANNEL EXPANSION

Introducing the change of variable (2.7), the Schrödinger equation (2.4) is transformed into:

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial\rho^2} - \frac{1}{2} \frac{1}{\rho} \frac{\partial}{\partial\rho} + H_0(\theta,\rho) \right] \psi(\theta,\rho) = E\psi(\theta,\rho) \tag{3.1}$$

where $H_0(\theta,\rho)$ is the quasivibrational part of the Hamiltonian in which ρ is a parameter:

$$H_0 = -\frac{1}{2} \frac{1}{\rho^2} \frac{\partial^2}{\partial\theta^2} + V(\theta,\rho) . \tag{3.2}$$

At fixed ρ one can use (2.9) and transform (3.2) to the form of a one-dimensional Hamiltonian in the variable $\underline{s}$.

$$H_0 = -\frac{1}{2}\frac{\partial^2}{\partial s^2} + V(s/\rho, \rho) \tag{3.3}$$

$$H_0 \chi_j(s, \rho) = \epsilon_j(\rho)\chi_j(s;\rho) \tag{3.4}$$

where the $\chi_i(s;\rho)$ can be taken as real, and $\int \chi_i(s;\rho)\,\chi_j(s;\rho)\,\rho\,d\theta$ equals δ_{ij} at fixed ρ. When ρ becomes large, we shall indicate whether s is in the range corresponding to the reactants' channel by writing

$$\chi_j(s;\rho) \to \chi_j^1(s;\rho) \cong \chi_j^1(y_1) \qquad (\rho \to \infty) \quad, \tag{3.5}$$

where $\chi_j^1(y_1)$ satisfies (2.5), or whether it is in the range corresponding to the products' channel by writing

$$\chi_j(s;\rho) \to \chi_j^2(s;\rho) \cong \chi_j^2(y_2) \quad. \tag{3.6}$$

For large ρ (3.2) reduces to a vibrational Hamiltonian for a diatomic molecule in the vicinity of a potential minimum, given by (2.5), when expressed in terms of (x, y) coordinates.

Since the solution of (3.2) for large ρ can be written in terms of the solutions of (2.5), one can seek a solution of (3.1) in a form which can be readily reduced to the form of the asymptotic solutions of (2.4) for large ρ, namely

$$\psi = \sum_j \phi_j(\rho)\,\chi_j(s;\rho) \tag{3.7}$$

which for large ρ can also be rewritten instead as (2.6). Wavefunctions $\eta_i(\theta;\rho)$, defined by

$$\eta_i(\theta;\rho) = \rho^{\frac{1}{2}}\chi_i(s;\rho) \quad, \tag{3.8}$$

with the normalization

$$\langle \eta_i | \eta_j \rangle = \int \eta_i \eta_j \, d\theta = \delta_{ij} \tag{3.9}$$

are next introduced.

Substituting (3.7) and (3.8) into (3.1), premultiplying by $\rho^{\frac{1}{2}} \eta_i(s;\rho)$, using (2.9) and integrating over θ one gets an infinite set of ordinary coupled differential equations in ρ for the coefficient functions $\phi_i(\rho)$

$$\left[-\frac{1}{2} \frac{d^2}{d\rho^2} - (E - \epsilon_i + \frac{1}{8\rho^2}) \right] \phi_i(\rho) + \sum_j (-i P_{ij} \frac{d}{d\rho} + \frac{1}{2} Q_{ij}) \phi_j(\rho) = 0 \ , \qquad (3.10)$$

where $P_{ij} = \langle x_i | - i \frac{d}{d\rho} | x_j \rangle$ \qquad (3.11)

$$Q_{ij} = \langle x_i | - \frac{d^2}{d\rho^2} | x_j \rangle \ . \qquad (3.12)$$

ϵ_i is given by Eq. (3.4) and the brackets denote integration over θ, as in (3.9).

Equation (3.10) is formally equivalent to the Schrödinger equation (2.4) or (3.1). By solving it[14] and imposing the scattering boundary conditions one can get the full scattering solution of (2.4). As shown in the next section however, for symmetric hydrogen atom exchange between two heavy atoms one can, at low energies, obtain a good approximate solution without solving coupled equations.

IV. SYMMETRIC HYDROGEN ATOM EXCHANGE

If atoms A and C are the same, the potential energy function $V(\rho, \theta)$ is symmetric about $\theta = \gamma/2$, and there are two distinct kinds of eigenfunctions of (3.3) which are symmetric and antisymmetric about $\theta = \gamma/2$, respectively. All the coupling elements (3.9) between the symmetric and the antisymmetric eigenfunctions x_i of (3.3) vanish by symmetry and the system (3.8) can be decoupled into two systems for the coefficients $\phi^s(\rho)$ and $\phi^a(\rho)$ of the symmetric and the antisymmetric wavefunctions $x_i(s, \rho)$, respectively.

$$\left[-\frac{1}{2} \frac{d^2}{d\rho^2} - (E - \epsilon_i^\beta + \frac{1}{8\rho^2}) \right] \phi_i^\beta(\rho) + \sum_{j=0}^{\infty} (P_{ij}^\beta \frac{d}{d\rho} + \frac{1}{2} Q_{ij}^\beta) \phi_j(\rho) = 0;$$

$$(\beta = s, a) \quad . \qquad (4.1)$$

Further, for collisions involving transfer of a hydrogen atom between two heavy atoms at low energies the Hamiltonian is nearly adiabatically separable in the coordinates ρ, θ and the coupling elements P_{oj}^β between the ground and the higher states of the same symmetry are expected to be small. In addition, at low energies near the reaction threshold only one state of each symmetry is open asymptotically, and the effective coupling P_{ij} to the classically forbidden states is weak. Since the Q_{ij} depend solely on the P_{ij}[14] the infinite sum in (4.1) can be neglected and the equation reduces to

$$\left[-\frac{1}{2} \frac{d^2}{d\rho^2} + \epsilon_0^\alpha - \frac{1}{8\rho^2} \right] \phi_0^\alpha = E \phi_0^\alpha \qquad (\alpha = s, a) \quad , \qquad (4.2)$$

where ϕ_0^α refers to ρ-motion for the lowest vibrational state of symmetry α.

The solution of (4.2) for large ρ yields the scattering solution of (3.1) in terms of the symmetric and antisymmetric ground state eigenfunctions of (3.3). The latter can be written as linear combination of the ground vibrational states of the reactants and products.

$$\chi_0^{s,a}(s;\rho) = \frac{1}{\sqrt{2}} [\chi_0^1(s;\rho) \pm \chi_0^2(s;\rho)] \quad . \qquad (4.3)$$

The $\chi_0^1(s,\rho)$ corresponds to the system being in the reactants', and $\chi_0^1(s;\rho)$ in the products' configuration. The s superscript in (4.3) refers to the plus sign.

For sufficiently large ρ the coordinates (s, ρ) can be made arbitrarily close to the Cartesian coordinates x_α, y_α in the region near the minimum of

the well in the reactant ($\alpha = 1$) or product ($\alpha = 2$) configuration. The vibrational wavefunctions $\chi_i^{1,2}$ (s;ρ) then reduce to the uncoupled vibrational wavefunctions of the reactants and the products, as in the second half of (3.5) and (3.6).

The wavefunction solution of (3.1) in the ground vibrational state

$$\psi(s,\rho) = \phi_0^S(\rho)\chi_0^S(s;\rho) + \phi_0^a(\rho)\chi_0^a(s;\rho) \tag{4.4}$$

can hence be written for large ρ, using (4.3), as

$$\psi(s,\rho) \sim \phi_0^1(\rho)\chi_0^1(s;\rho) + \phi_0^2(\rho)\chi_0^2(s;\rho)$$

$$\sim \phi_0^1(x_1)\chi_0^1(y_1) + \phi_0^2(x_2)\chi_0^2(y_2) \quad . \tag{4.5}$$

Comparing (4.3), (4.5), (3.5) and (3.6) one can write for large ρ

$$\phi_0^{1,2}(x_{1,2}) \sim \frac{1}{\sqrt{2}}\left[\phi_0^S(\rho) \pm \phi_0^a(\rho)\right] \quad , \tag{4.6}$$

where the 1 superscript refers to the plus sign.

Writing the asymptotic solution of (3.1) in terms of an S-matrix

$$\psi = (e^{-ikx_1} + S_{00}^N e^{ikx_1})\chi_0^1(y_1) + S_{00}^R e^{ikx_2}\chi_0^2(y_2) \quad , \tag{4.7}$$

where S_{00}^N and S_{00}^R are the amplitudes of the nonreactive and reactive outgoing waves, respectively, i.e., the nonreactive and reactive S-matrix elements, one obtains

$$S_{00}^N = \frac{1}{2}(e^{2i\xi_0^S} + e^{2i\xi_0^a}) = e^{i(\xi_0^S + \xi_0^a)}\cos(\xi_0^S + \xi_0^a) \tag{4.8}$$

$$S_{00}^R = \frac{1}{2}(e^{2i\xi_0^S} - e^{2i\xi_0^a}) = e^{i(\xi_0^S + \xi_0^a)}\sin(\xi_0^S - \xi_0^a) \quad , \tag{4.9}$$

where ξ_0^S, ξ_0^a are the elastic phase shifts obtained by solving (4.2).

The zero order approximation to the reactive transition probability in a symmetric collinear hydrogen atom exchange collision is hence given by

$$P_{00}^R = \left| S_{00}^R \right|^2 = \sin^2(\xi_0^S - \xi_0^a) \quad . \tag{4.10}$$

Equation (4.10) is the same as the expression for the S-matrix elements in case of exact resonance in atomic collisions involving transfer of an electron or electronic excitation between two identical atoms. [15]

Equation (4.10) is the desired expression for the probability of transferring a light particle in a low energy collinear collision based on the adiabaticity of the light particle vibration throughout the collision. In order to obtain numerically the values of the transition probability as given by (4.10) as a function of energy at low energies one needs to solve first for the two lowest eigenvalues $\epsilon_0^{S,\,a}(\rho)$ of H_0, Eq. (3.3), for several values of the parameters ρ and then evaluate the phase shifts $\xi_0^{S,\,a}$ for scattering on the effective potentials $\epsilon_0^{S,\,a}$ for the heavy particle motion along ρ by solving Eq. (4.2) at the desired energies.

Some numerical results of applying Eq. (4.10) are given in Sec. VI. In the next section we evaluate the semiclassical limit of the quantum mechanical result (4.10), thereby exhibiting some of the relevant aspects of the collision dynamics in a more intuitive, semiclassical way. (Cf also Sec. VII.)

V. SEMICLASSICAL LIMIT OF THE TRANSITION PROBABILITIES EXPRESSION

If the potential energy surface for the collinear symmetric hydrogen exchange $V(s;\rho)$ has a sufficiently large barrier the reaction will at low energies proceed by tunneling and the probability for reaction at energies

below the classical threshold will be nonzero but small. All the quantities
needed for calculating the transition probability in (4.10) for those energies
can be evaluated semiclassically.

The "vibrational" potential energy curve $V(s;\rho)$ will be a double minimum
potential as a function of s for all the values of ρ relevant for determining the
reaction probabilities in the tunneling region. Moreover, both the lowest sym-
metric and the lowest antisymmetric eigenvalue of the double-well potential
will be below the barrier maximum (Fig. 2) so that a simple semiclassical
approximation can be used for their evaluation. The semiclassical condition
for determining the lowest pair of eigenvalues of a symmetric double-well
potential below the top of the barrier is given by[16, 17]

$$\int_{s_1}^{s_2} p(s;\rho)\, ds = \pi/2 \pm e^{-Q(\rho)} \tag{5.1}$$

where

$$Q(\rho) = \int_{s_2^0}^{s_3^0} p(s;\rho)\, ds, \quad p(s;\rho) = |2[\epsilon(\rho) - V(s;\rho)]|^{\frac{1}{2}} \quad . \tag{5.2}$$

The s_i denote the turning points for the motion on the double-well potential
(Fig. 2) and are slightly different for the + and - states in (5.1). The s_i^0
denote the turning points for the motion in each of the two separate single-well
potentials (Fig. 2). The mean energy of the first two eigenvalues, which will be
denoted by $\epsilon_0(\rho)$ is in the limit of small splitting given by the usual semiclassical
eigenvalue condition for a single well potential[18]

$$\int_{s_1^0}^{s_2^0} p(s;\rho)\, ds = \pi/2 \tag{5.3}$$

Their splitting is given by[16, 17]

$$\epsilon^a(\rho) - \epsilon^s(\rho) = \frac{2}{\pi} E_0(\rho)\, e^{-Q(\rho)} \quad . \tag{5.4}$$

Here, $E_0(\rho)$ is the ground state eigenvalue for a single well potential as
determined by (5.3). $E_0(\rho)$ is measured from the bottom of the well, i.e.,

$E_0(\rho) = \epsilon_0(\rho) - V_{min}(s;\rho)$. The energy splitting of the eigenvalues of symmetric double well potential is hence proportional to the tunneling amplitude from one well to the other $\exp[-Q(\rho)]$.

If the barrier on the potential energy surface is sufficiently large both the symmetric and the antisymmetric eigenvalues $\epsilon^{s,\,a}(\rho)$ will change monotonically with increasing ρ and the elastic phase shifts for scattering on $\epsilon^s(\rho)$ and $\epsilon^a(\rho)$ can be evaluated semiclassically as

$$\xi^\beta = p^\beta(\rho)\rho - \int_{\rho_\beta}^{\rho} p^\beta(\rho')d\rho' : \qquad (\beta = s, a) \quad , \tag{5.5}$$

where $p^\beta(\rho) = \{ 2[E - \epsilon^\beta(\rho)]\}^{\frac{1}{2}}$ and ρ_β is the classical turning point on the effective potential $\epsilon^\beta(\rho)$ for the ρ motion. The difference of the elastic phase shifts, which determines the reactive transition probability in (4.10), is then

$$\xi^s - \xi^a = \int_{\rho_s}^{\rho} p^s(\rho)d\rho - \int_{\rho_a}^{\rho} p^a(\rho)d\rho : \qquad \rho \to \infty \quad . \tag{5.6}$$

A difference of phase integrals similar to (5.6) appears in the semiclassical treatment of curve crossing problems and is often approximated by,[19]

$$\xi_0^s - \xi_0^a = \int_{\rho_0}^{\rho} \frac{1}{p_0(\rho)} [\epsilon^a(\rho) - \epsilon^s(\rho)]d\rho \tag{5.7}$$

where $p_0(\rho) = \{ 2[E - \epsilon_0(\rho)]\}^{\frac{1}{2}}$ and ρ_0 is the value of ρ at the classical turning point of the "mean" potential energy curve $\epsilon_0(\rho)$. Equation (5.7) is often referred to[19] as the "classical path" approximation since it leads to results similar to those obtained by assuming the existence of the time dependent classical path $\rho(t)$. The assumptions used in obtaining (5.7) are however

less stringent than the assumption of the existence of a time-dependent classical path for the ρ motion. [19c]

Using (5. 4) and (5. 10) can be written as

$$P_{00}^R = \sin^2(\xi_0^S - \xi_0^a) \cong (\xi_0^S - \xi_0^a)^2 \qquad (5. 8)$$

where

$$\xi_0^S - \xi_0^a = \frac{2}{\pi} \int_{\rho_0}^{\infty} \frac{E_0(\rho)}{p_0(\rho)} e^{-Q(\rho)} d\rho \qquad . \qquad (5. 9)$$

Equation (5. 9) gives the semiclassical limit of the hydrogen atom exchange probability P_{00}^R as an integral of the hydrogen atom tunneling amplitude over the configuration space of the heavy atoms. A further physical insight into the structure of (5. 9) can be obtained by the explicit introduction of the classical path approximation as shown in Sec. VII.

We next proceed to evaluate the integral in (5. 9) approximately. Typically $e^{-Q(\rho)}$ will decay with increasing ρ sufficiently rapidly so that the integral above is determined by the values of the integrand in a narrow region around the classical turning point for the heavy particles motion ρ_0. In the vicinity of ρ_0 the slowly varying vibrational eigenvalue $E_0(\rho)$ can be approximated by its value at the turning point, E_0^0. Both $p_0^2(\rho) = 2[E - \epsilon_0(\rho)]$ and $Q(\rho)$ are next approximated by their power series expansions around ρ_0 truncated at the linear term. Thus,

$$E_0(\rho_0) \cong E_0^0 \qquad (5. 10a)$$

$$p_0^2(\rho) = 2(\rho - \rho_0)\epsilon_0' ; \quad \epsilon_0' = -\left[\frac{d\epsilon_0(\rho)}{d\rho}\right]_{\rho=\rho_0} \qquad (5. 10b)$$

$$Q(\rho) = Q_0 + (\rho - \rho_0)Q_0' ; \quad Q_0' = \left[\frac{dQ(\rho)}{d\rho}\right]_{\rho=\rho_0} \qquad , \qquad (5. 10c)$$

where Q_0 denotes $Q(\rho_0)$. Substituting (5. 10) into (5. 9) and performing the integration one obtains

$$(P_{00}^R)^{\frac{1}{2}} = |S_{00}^R| \cong \xi_o^s - \xi_o^a = \frac{\sqrt{2}\ E_o^0}{(\pi\epsilon_o'Q_o')^{\frac{1}{2}}}\ e^{-Q_o} = \gamma\epsilon^{-Q_o} \quad , \tag{5.11}$$

where γ is defined by the right-hand equality in (5.11), Q_0 is given by
(5.2) evaluated at $\rho = \rho_0$ and $\epsilon_0(\rho)$ is defined as the eigenvalue satisfying (5.3).
Equation (5.11) is given also in Ref. 7, with a slightly different tunneling path
and $\epsilon_0(\rho)$ function (polar coordinates were not used).

The reactive transition amplitude is hence given by the penetration
amplitude for the hydrogen atom tunneling e^{-Q_o} at the classical turning point of
the heavy particles multiplied by a preexponential factor γ.

VI. NUMERICAL TESTS

The reactive transition probabilities as a function of the collision
energy were evaluated for two different LEPS potential energy surfaces. The
first one was chosen using as asymptotic parameters[20a] those for the F + HF →
FH + F reaction. Three different Sato parameters 0.15, 0.1 and 0 were used
to obtain surfaces with a low (~1.5 kcal), moderate (~6 kcal) and high (~19 kcal)
barrier at the saddle point. These three surfaces will be denoted as surfaces
1a, 1b and 1c, respectively. Only the last one has a barrier height which
roughly corresponds to the expected barrier for the reaction;[20b] the other two
were included to examine the influence of the barrier height on the reaction
dynamics. The second surface has parameters chosen to simulate the
$CH_4 + CH_3 \rightarrow CH_3 + CH_4$ reaction. The asymptotic parameters are the same as
those of Ref. 7a and the Sato parameter was chosen to be s = 0.185.[21] The
resulting barrier at the saddle-point is 13.8 kcal.

The quasi-vibrational eigenvalues, i.e., the eigenvalues of (3.3) were
evaluated using the finite element method of Malik, Eccles and Secrest.[22]

The first two symmetric and antisymmetric state eigenvalues are shown in Fig. 3 as a function of ρ for surface 1b.

The present approximation to the reactive transition probability (4.10) was obtained by solving (4.2) numerically using Gordon's method[23] to obtain the elastic phase shifts. The reactive transition probability as a function of the total energy is shown in Fig. 4 for surface 1a, b, c and in Fig. 5 for surface 2. This transition probability as a function of energy is shown on a logarithmic scale in the tunneling region in Figs. 6 and 7. Some classical trajectory results for the moderate barrier surface 1b are also shown in Fig. 4.

A method well-suited for performing accurate quantum mechanical calculations involving a symmetric hydrogen atom exchange between two heavy atoms (or any atom diatomic molecule reaction) has been developed by Kuppermann, Kaye and Dwyer.[13a, b] The results of the present approximation for the systems studied here are in good agreement with preliminary results obtained using that method.[13c] In particular, the shape of the transition probability vs. energy curve for all the systems studied is reproduced quite accurately. The features included in this curve are the peaks for surface 1a, b due to shape resonances in the solution of (4.2)[26, 27] and the large oscillations (Figs. 4c, 5) due to smooth increases of the phase difference in (4.10) through 2π. There is a small shift of 0.04 - 0.12 kcal/mole of the approximate curve in Figs. 5-8 toward the lower energy relative to the coupled channel ————————————————

results in the threshold region. The shift increases at higher energies, particularly for the low barrier reactions. Even smaller shifts can be expected for collisions in which a hydrogen atom is transferred between still heavier atoms. In contrast, for the collisions of the X + HX series, where X is a hydrogen atom isotope for which accurate coupled channel results exist,[13a, d] the corresponding shifts are much larger (0. 5 to 1. 0 kcal in the threshold region).[24]

VII. DISCUSSION

The results presented in the preceeding section indicate that there is an effective adiabatic separation between the fast hydrogen atom vibration and the slow translation of heavier atoms in hydrogen atom exchange reactions at energies near the reaction threshold. The polar coordinates used here are sufficiently close to the dynamical variables between which the optimum adiabatic separation exists at any point in the reaction, and so are useful for these approximate calculations.

At energies at which only the ground vibrational state is asymptotically open, the reaction transition probability for a symmetric exchange reaction can always be written rigorously in the form (4. 10) if one replaces the adiabatic phase shifts $\xi_0^{S, a}$ obtained by solving Eq. (4. 3) by the exact phase shifts [25] which in the present formulation can be obtained by solving (4. 2). However, only for the transfer of a light particle between two heavy ones are the polar coordinates sufficiently close to the optimally separable ones and (4. 10) then provides a good approximation to the transition probabilities.

The principal approximations in the analysis leading to Eq. (4. 10) are (i) neglect of nonadiabatic effects and (ii) use of polar coordinates to

treat the dynamics. Each could be improved, e. g., in (i) by including perturbatively a nonadiabatic correction to an elastic phase shift in (4. 2), particularly in the case of any near avoided crossing of the $\epsilon_0^S(\rho)$ and $\epsilon_1^S(\rho)$ curves. However, for the present mass ratios the current approximations are seen to be quite adequate for the systems treated.

A distinct feature of the hydrogen atom or proton transfer reaction between two heavy atoms on potential energy surfaces with high barriers is, as shown in Figs. 5c and 6, the unusually large amount of tunneling, i. e., there is an appreciable reaction probability when the total energy of the reaction is below the top of the saddle point barrier. For reactions with different mass combinations for which the characteristic angle γ in Eq. (2. 3) is much closer to 90° can be, at least qualitatively, understood in terms of natural collision coordinates.[1] The vibrational motion in those coordinates is perpendicular to the reaction coordinate and the part of energy tied up as vibration is unavailable for crossing the barrier. In the present case the vibrational coordinate is parallel to the reaction coordinate (see Fig. 1) only in the region of closest approach, and is utilized in surmounting the barrier between the reactant and the product channel.

We now turn to the semiclassical expression (5. 9).[28] This expression points to an intuitive way of understanding the physical factors which determine the transition probability in the tunneling region. The value of the transition probability in the tunneling region in (5. 11) is determined mainly by the amplitude for the hydrogen atom tunneling in one dimension across the ridge between the two channels at the classical turning point for the heavy particle motion, given by e^{-Q_0}. The preexponential factor γ is, for the systems 1b, 1c and 2, within a factor of five

from unity and depends on the characteristics of a particular surface.

Equation (5.11) can also be obtained by treating the heavy particle motions classically and the hydrogen atom motion quantum mechanically. The approach used above, however, yield the same result without the restrictive assumption of existence of a time-dependent classical trajectory for the heavy particle motion. The classical path picture can nevertheless be used to gain additional insight into the structure of (5.9) and into the nature of the preexponential factor in (5.11). If, starting from (5.9), one introduces explicitly a classical trajectory $\rho(t)$ for the classical motion of the heavy atoms on the one-dimensional mean potential curve $\epsilon_0(\rho)$ the local heavy particle velocity and momentum can be written as

$$p_0(\rho) = v_0(\rho) = d\rho/dt \quad (m = 1) \quad . \tag{7.1}$$

The local vibrational energy $E_0(\rho)$, can be written in terms of the vibrational frequency $\frac{1}{2}h\nu$, i. e., in terms of the vibrational period as

$$E_0[\rho(t)] = \pi/\tau[\rho(t)] \quad (\hbar = 1) \quad , \tag{7.2}$$

where τ is the vibrational period of the s motion for a given $\rho(t)$ and hence for a given t. Substituting (7.1) and (7.2) into (5.9) one obtains

$$|S_{00}^R| = \int_{-\infty}^{\infty} e^{-Q(t)} \, dt/\tau \quad . \tag{7.3}$$

(A factor of 2 in (5.9), and symmetry about the time of closest approach $[Q(t) = Q(-t)]$ results in the integration limits being $-\infty$ to $+\infty$ instead of $-\infty$ to 0.)

According to (7.3) the reactive transition amplitude can be obtained by integrating over the time-dependent tunneling amplitude for tunneling of the hydrogen atom into the product region over the time of approach and

separation of the heavy particles.

Equation (7.3) is a classical path approximation. However, it can be used to obtain a semiclassical tunneling correction for use of an ensemble of purely classical trajectories below the classical threshold as follows. Dividing the integration range in (7.3) into increments over one vibrational period each one obtains

$$|S_{00}^R| = \sum_i \int_{t_i}^{t_i+\tau_i} e^{-Q(t)} \, dt/\tau \tag{7.4}$$

Integrating $d(t/\tau)$ over an interval $t_i + \tau_i$ in Eq. (7.4) corresponds in an ensemble of trajectories to averaging over the initial vibrational phase (classical angle variable). Thereby Eq. (7.4) becomes

$$|S_{00}^R| \cong \left\langle \sum_{i=1}^{\infty} e^{-Q_i} \right\rangle \tag{7.5}$$

where the brackets $\langle \, \rangle$ indicate an average over the initial vibrational phase and Q_i denotes the value of $Q(t)$ at the i'th inner vibrational turning point (i.e., the point closest to the products' region), whose ρ-value in turn varies with initial vibrational phase.

Hence, the reactive transition amplitude can be obtained from an ensemble of purely classical trajectories by summing the amplitudes for tunneling into the product region at every inner vibrational turning point during the approach of the reactants and during their separation.

In spite of the additional approximations used in deriving Eq. (7.5), the latter could give better results for the transition probability in the tunneling region than the quantum expression (4.10. The use of exact classical mechanics provides a more accurate description of the ρ-s dynamics within a channel than the decoupling approximation, clearly at the price of the

additional effort needed to solve for the classical dynamics exactly.

Another advantage of Eq. (7. 5) is that its use can straightforwardly albeit heuristically be extended to multidimensional systems in order to obtain an approximation for the tunneling corrections to the results of purely classical trajectory studies. The increasing complications with systems with many degrees of freedom make the exact quantum calculations computationally difficult at the present time, while the classical trajectory studies can be done more easily.

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26. Resonance peaks in the P_{00}^R vs. energy curve due to potential energy wells in the vibrationally-excited $\epsilon_i^\beta(\rho)$ curves (upper curves in Fig. 3) can be expected to play a role at somewhat higher energies, for the low and moderate barrier surfaces. They are not included in Eq. (4.10).

27. Resonances in the symmetric isotopic H + H_2 reaction have been studied in Ref. 13a using polar coordinates.

28. The resonance peaks in Fig. 5a, b and 7 are not reproduced by the present semiclassical results given by (5.11), due to the use of the simple one-turning point formula for the phase shift (5.5). For the case when the effective potential $\epsilon_0^S(\rho)$ has a barrier and can have three turning points at some energies the appropriate semiclassical formula[16, 29, 30] includes another additive "resonant" term. Althrough this term can be included in the derivation in Sec. V, it was omitted to avoid obscuring the main point of Sec. V, which is to illuminate the role of the tunneling by the H-atom across the ridge between the two channels (i.e., along the s-coordinate). Including the "resonant" term in (5.5) would, on the other hand, reflect the heavy particle tunneling (tunneling along ρ) in the dynamics. The latter does not, except at the resonance energies, contribute much to the reaction probability.

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FIGURE CAPTIONS

Figure 1. A potential energy contour plot of the surface 1b in mass-weighted coordinates. Several values of the contours are listed in kcal. A reactive classical trajectory with energy 8. 93 kcal, slightly above the classical threshold, is also shown (dashed line). The sudden jump of the trajectory from the reactants' to the products' region well before reaching the saddle point is characteristic for transfer of a light particle between two heavy ones. This is in contrast to the usual picture of a vibrationally adiabatic collision in which the trajectory winds along the minimum potential energy path. Most trajectories are less symmetric than the one shown.

Figure 2. A cut through the potential energy function $V(s, \rho)$ for ρ = 13.7 on surface 2; semiclassical (WKB) single-well eigenvalue $\epsilon_0(\rho)$, as determined by Eq. (5. 3) (full line) ; semiclassical approximation to the symmetric and the antisymmetric double minimum eigenvalues, given by Eq. (5. 1) (dashed lines). The points s_i and s_i^0 are defined in the text.

Figure 3. The first two symmetric and antisymmetric diagonal matrix elements $\epsilon_i^\beta(\rho)$ (Eq. 4. 3) for surface 1b (moderate barrier surface with F + HF asymptotic parameters).

Figure 4. The ground vibrational state reactive transition probability P_{00}^R (Eq. 4.10) (full line) as a function of total energy for surfaces 1a, b, c (FH + F with low, moderate and high saddle-point barrier). The vertical arrows on the abscissa denote the saddle-point barrier heights for surfaces b and c. The a curve has two sharp peaks as indicated. Some purely classical trajectory results for the moderate barrier surface 1b in the threshold region are also shown (dashed line).

Figure 5. The ground vibrational state reactive transition probability P_{00}^R for surface 2 ($CH_3 + CH_4 \rightarrow CH_4 + CH_3$). The vertical arrow on the abscissa denotes the saddle-point barrier height.

Figure 6. Logarithm of the reactive transition probability P_{00}^R vs. total energy (Eq. 4.10) for surface 1b.

Figure 7. Logarithm of the transition probability P_{00}^R vs. total energy (Eq. 4.10) for surface 2.

Figure 1

x₁ (mass weighted a.u.)

Figure 2

Figure 3

$F + HF \longrightarrow FH + F$

Figure 4

Figure 5

moderate
barrier FH + F

Total Energy (kcal)

$-\log P_{00}^{R}$
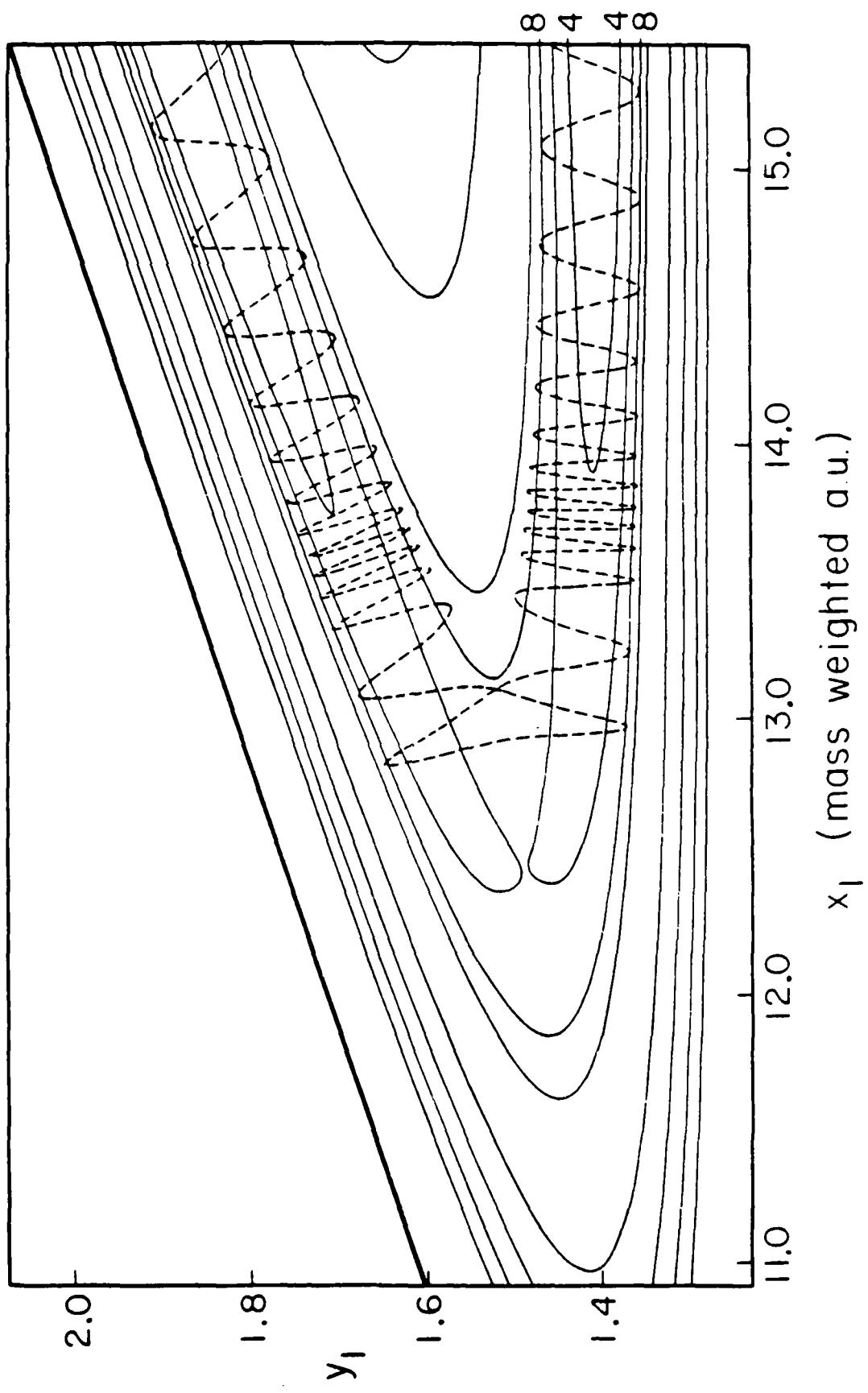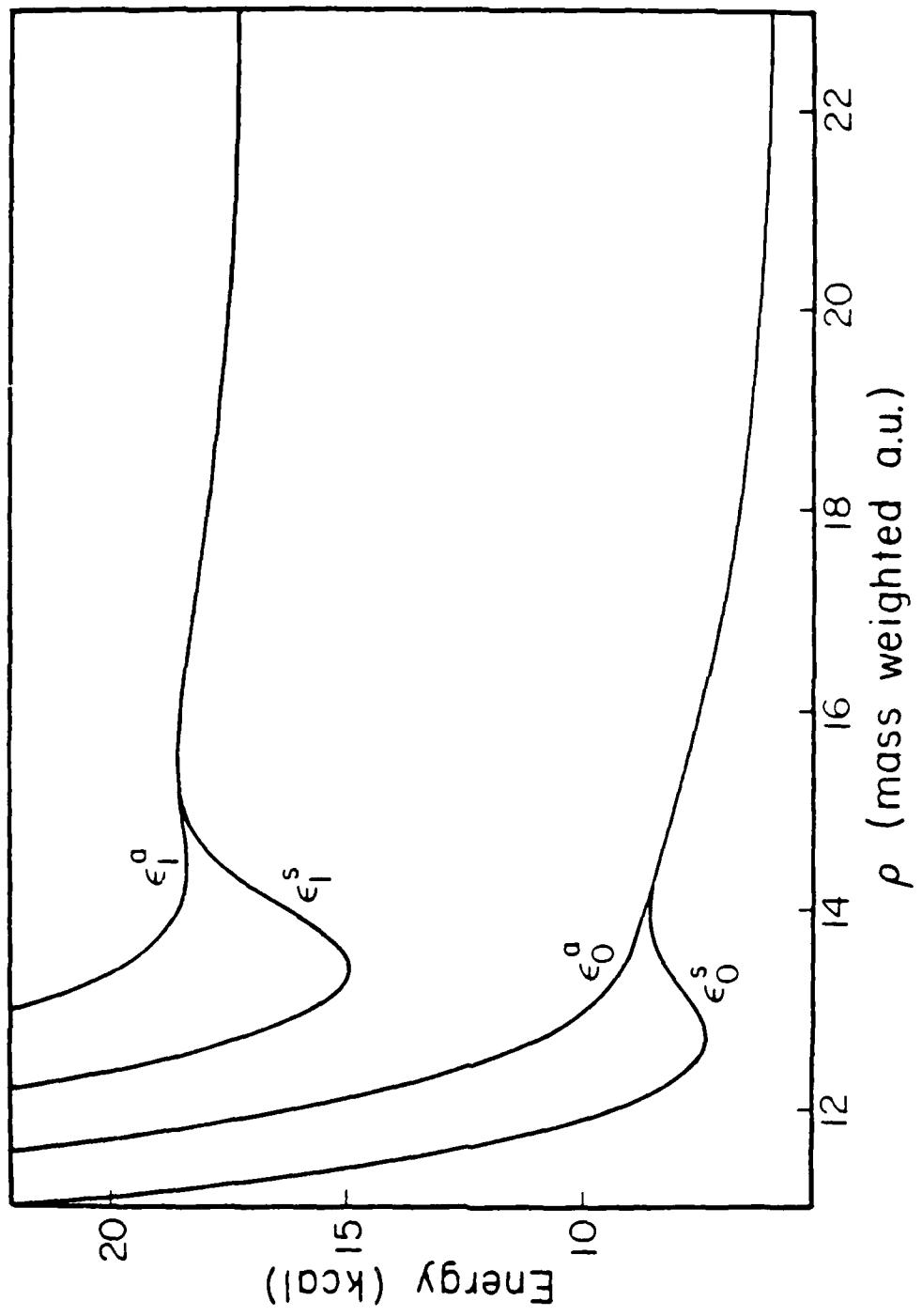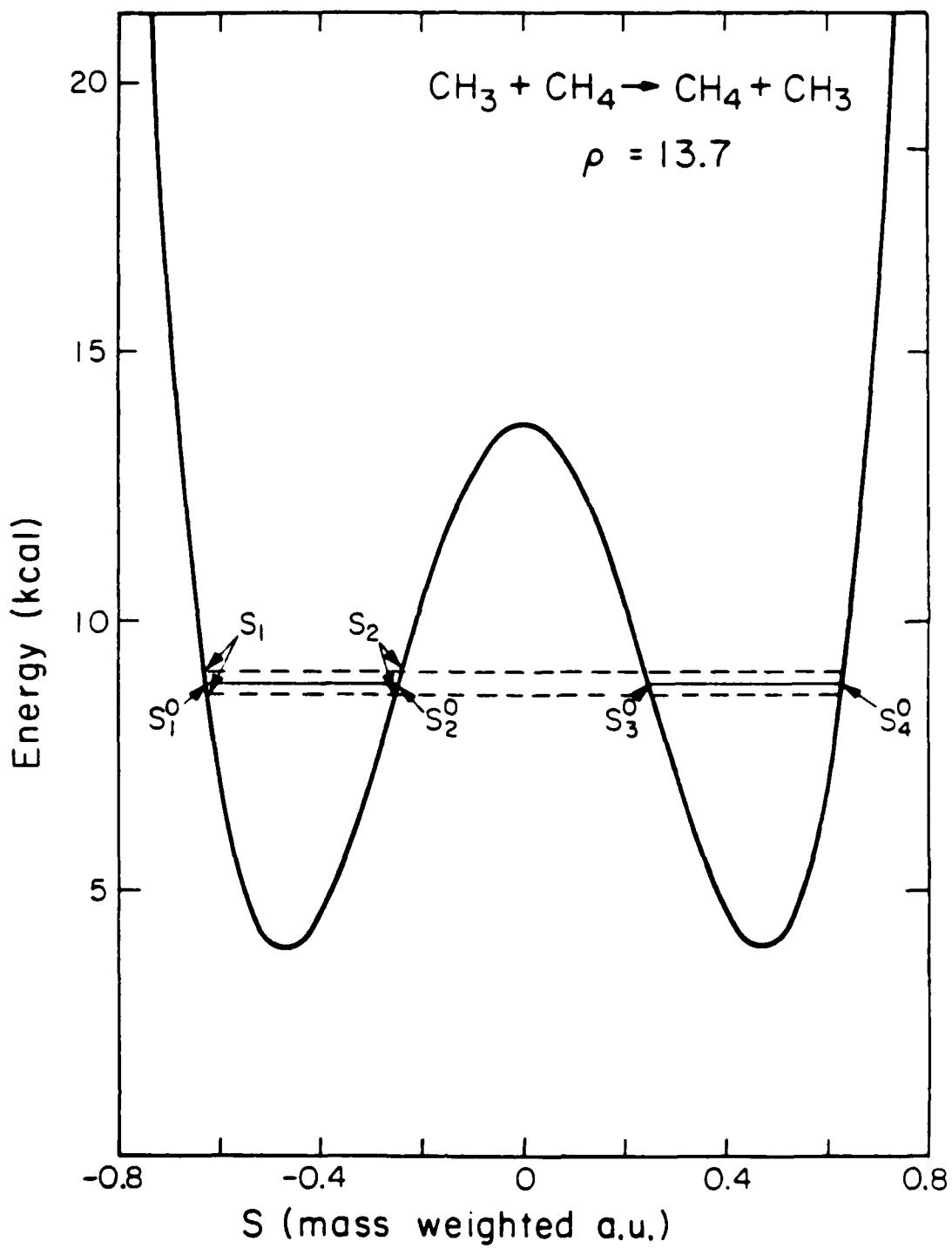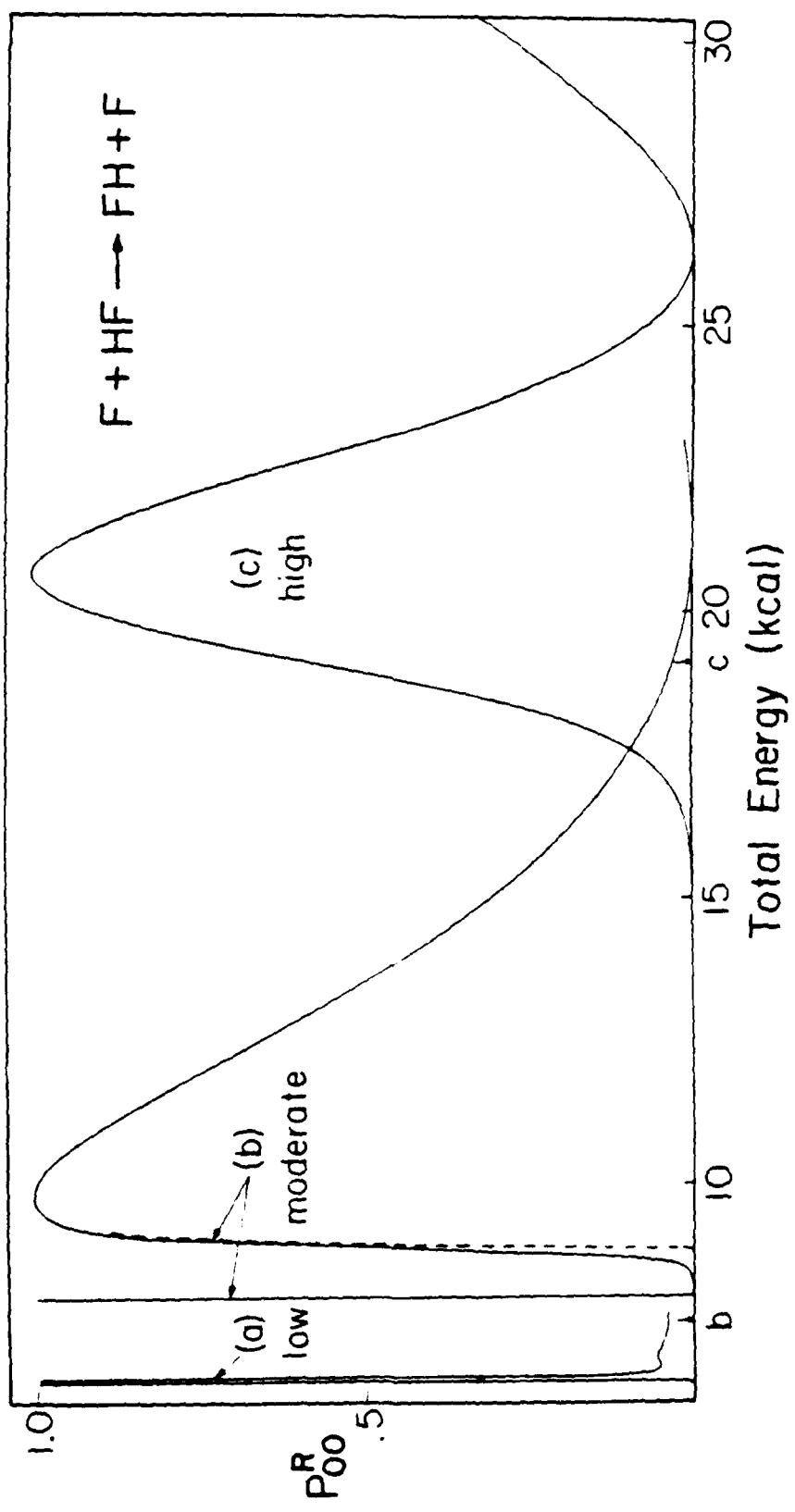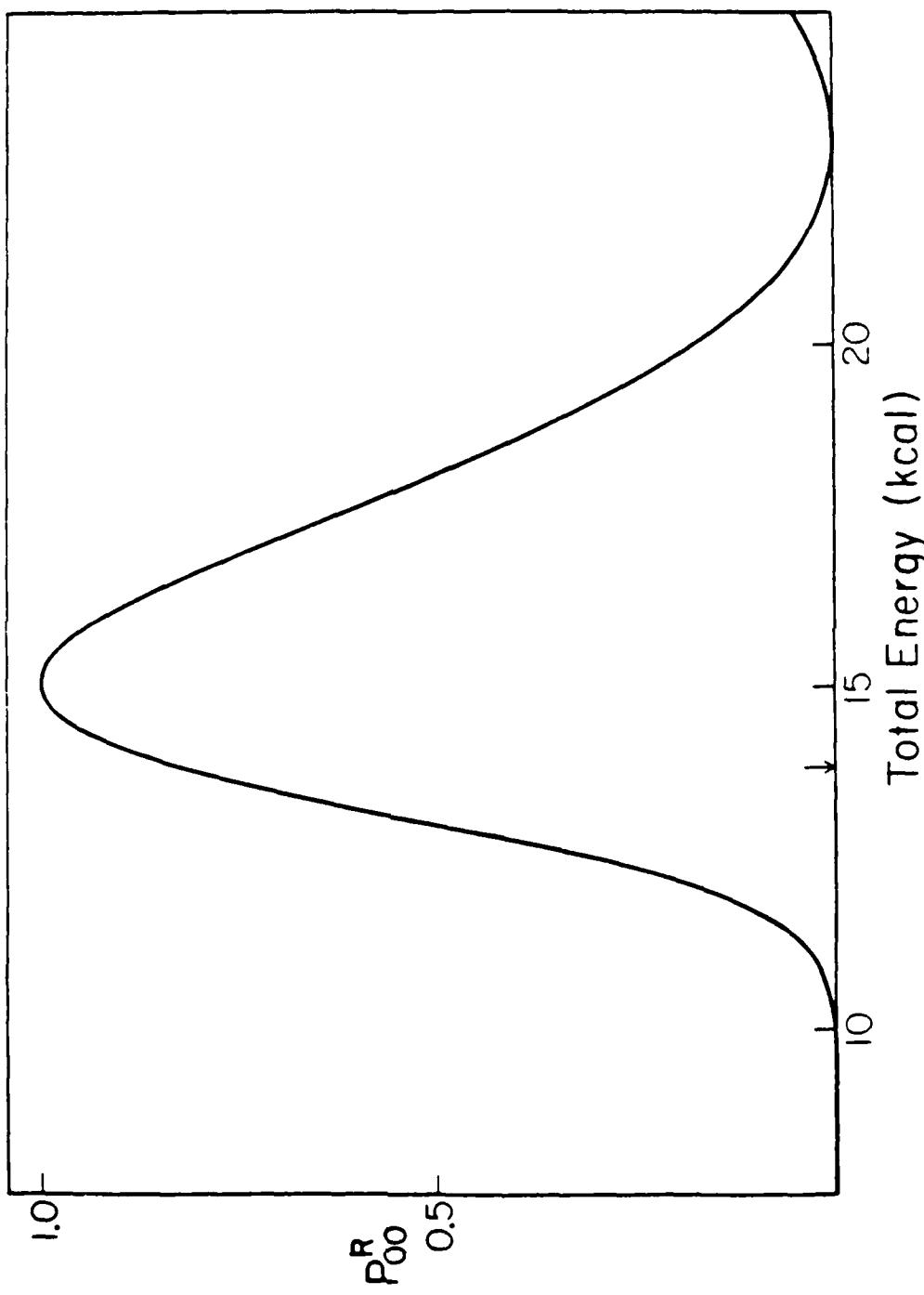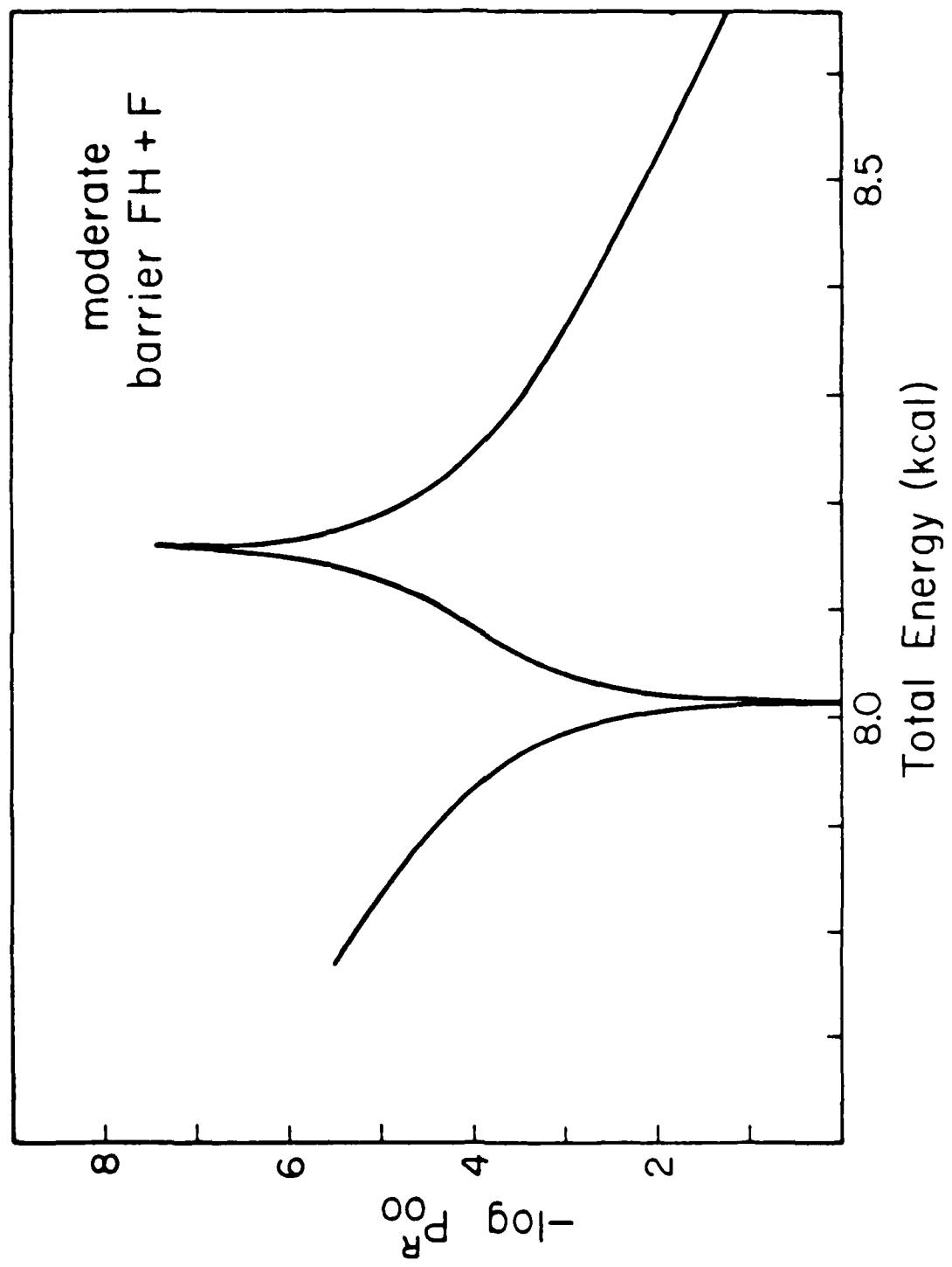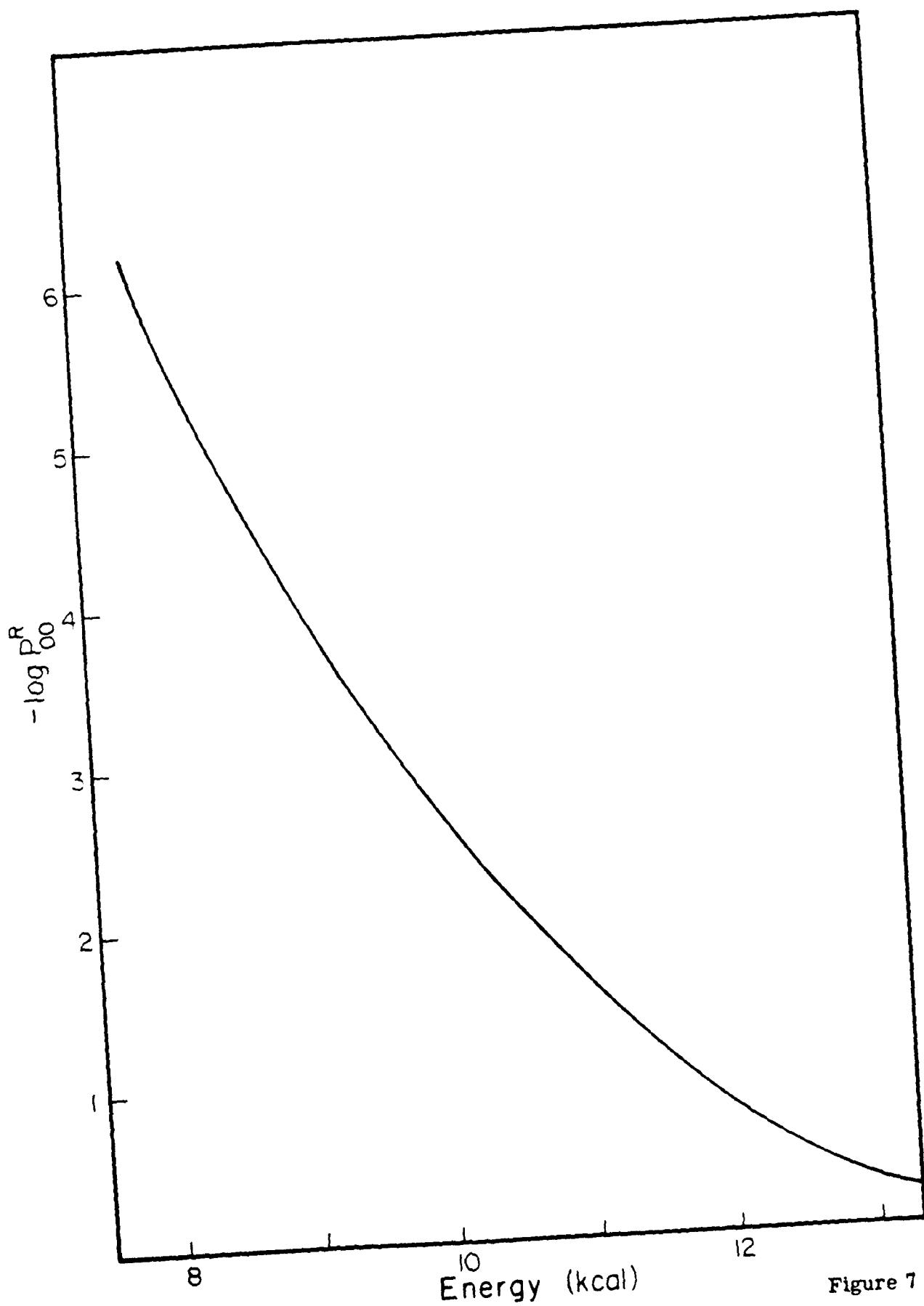
Figure 6

Figure 7

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